

Anomalous carrier density independent superconductivity in iron pnictides

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Dome-shape superconductivity phase diagram can commonly be observed in cuprate- and iron-based systems via tuning parameters such as charge carrier doping, pressure, bond angle, and etc. We report doping electrons from transition-metal elements (TM = Co, Ni) substitution can induce high- T_c superconductivity around 35 K in $\text{Ca}_{0.94}\text{La}_{0.06}\text{Fe}_2\text{As}_2$, which emerges abruptly before the total suppression of the innate spin-density-wave/anti-ferromagnetism (SDW/AFM) state. Unexpectedly, the onset critical temperature for the high- T_c superconductivity stays constant for a wide range of TM doping. Possible extrinsic factors like phase separation, chemical inhomogeneity, and charge carrier cancelation effect are all excluded. This anomalous charge carrier density independent SC is very similar to the interface superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ - La_2CuO_4 bilayer system. The further verified two-dimensional (2D) nature of superconductivity by the Tinkham's angular-dependent critical field model as well as by the angle-resolved magneto-resistance measurements jointly supports the idea of interfacial effect induced high- T_c superconductivity.

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The recent observation of high- T_c superconductivity over 100 K in FeSe monolayer film has renewed the interests in Fe-based superconductor (IBSs) studies^{1,2}. A focus debate ever since its discovery was whether the interfacial effect plays an important role on the giant enhancement of T_c in comparison with FeSe bulk. Interfacial effect enhanced T_c has been commonly reported in cuprate-based heterostructures³⁻⁵. To explain the phenomenon of interface-induced T_c enhancement, many models have been proposed^{4,6-8}. In all models, strong carrier density dependent T_c would be expected⁸. However, this simple principle which both experimentalists and theorists keep following has recently been challenged by the interface superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ - La_2CuO_4 bilayer⁴. It is reported the critical superconducting transition temperature stays essentially constant across a wide doping range, $0.15 < x < 0.47$. This surprising results were extracted from an unprecedentedly large set of more than 800 different compositions, which strongly guarantees the experiment repeatability and reliability. This anomalous charge carrier doping independent interface superconductivity poses a big challenge to the ordinary Fermi liquids because a carrier-doping independent chemical potential has to be supposed in its possible explanation.

We report that the similar awkward situation occurs in another system of iron-based compounds, rare-earth-element-doped CaFe_2As_2 . Due to the big T_c difference between $(\text{Ca}, \text{RE})\text{Fe}_2\text{As}_2$ ($\text{RE} = \text{rare earth element}$) and its counterparts bearing structural and chemical similarities as well as the extremely large magnetic anisotropy, interface effect has previously been proposed for the high- T_c superconductivity origin⁹⁻¹¹. If this assumption is true, $(\text{Ca}, \text{RE})\text{Fe}_2\text{As}_2$ system should be the first evidence of interface superconductivity in bulks, which will certainly bring new clues in searching and understanding high- T_c superconductivity. However, further strong evidences for interface superconductivity in $(\text{Ca}, \text{RE})\text{Fe}_2\text{As}_2$ is still lack. Through electron doping from TM substitution, we discovered that the primary under-doping $\text{Ca}_{0.94}\text{La}_{0.06}\text{Fe}_2\text{As}_2$ without high T_c can be triggered to show superconductivity around $T = 35$ K. Unpredictably, as the case of interface SC in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ - La_2CuO_4 bilayer, the high T_c value stays essentially constant against a wide range of TM doping. Benefitted from the easy achievement of TM substitution, a universal and complete electron-doping-dependent high- T_c phase diagram (high- T_c window closed) $T_c(n)$ is established, where n is the net extra doping electron number. The possible extrinsic pitfalls for the strange carrier density independent T_c have been excluded by systematic structural and elemental analysis as well as abundant transport measurements. Simultaneously, through angle-

and magnetic field- dependent transport measurement, we give evidence of two-dimensional (2D) SC nature from Tinkham's model of angular-dependent critical field for sufficiently thin films¹². These experimental data strongly support the existence of interfacial effect in the occurrence of high- T_c superconductivity.

Single crystals of $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{TM}_x)_2\text{As}_2$ were grown by FeAs self-flux method as reported before^{13,14}. Special attention was paid during the weighting of starting materials to achieve a precise control of the La and TM doping levels. The quality of the obtained crystals has been checked by single crystal X-ray diffraction (XRD) measurement (Supplementary information (SI), S1). Elemental analyses were carried out by energy-dispersive X-ray (EDS) spectroscopy on a field emission scanning electron microscopy (SEM). To accurately determine the doping levels, the compound compositions were determined by average of the multi-point EDS measurements on each crystal. The electrical transport data were obtained by standard four-probe method. For Hall measurements, to cancel the electrode symmetric factor, Hall resistivity is calculated via formula $\rho_{xy} = [\rho_{xy}(\mu_0 H > 0) - \rho_{xy}(\mu_0 H < 0)]/2$.

Figs. 1(a) and (b) show the EDS results. The actual TM doping levels are very close to the nominal values. And as expected, the La doping level keeps invariable as TM doping level x increases. Figs. 1 (c-f) show the corresponding temperature dependence of resistivity (RT) for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{TM}_x)_2\text{As}_2$ crystals with different x values, in which the resistivity (ρ_N) has been normalized by its value at 300 K. Without TM doping, a SDW transition with a resistivity upturn at $T_s \sim 150$ K and a low- T_c superconducting transition around 10 K can be identified. As x increases, T_s is gradually suppressed. Simultaneously, SC with high- T_c around 35 K emerges suddenly before the total suppression of SDW state (Diamagnetic signal for 35 K superconductivity is shown in SI, S2). It should be pointed out that the high- T_c SC doesn't directly evolve from the low- T_c phase in low doping levels but emerges abruptly, in stark contrast to the TM doping phase diagrams in many IBSs^{15,16}.

The doping level dependence of the higher superconducting transition T_c is plotted in Figs. 2. Intriguingly, for both the cases of Co and Ni doping, the high- T_c superconducting transition starts at an onset temperature around 35 K and keeps essentially constant for a large TM doping range (see Fig. 2 (a) and (b)). This special range almost covers the superconducting dome in TM-doped BaFe_2As_2 or CaFe_2As_2 ^{15,17,18} (see Fig. 2 (c)). In fact, the similar T_c -constant behavior has also been noticed in TM-free $\text{Ca}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2$ crystals (shown in SI, S3) and in pressure experiments on under-doping $\text{Ca}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2$ if

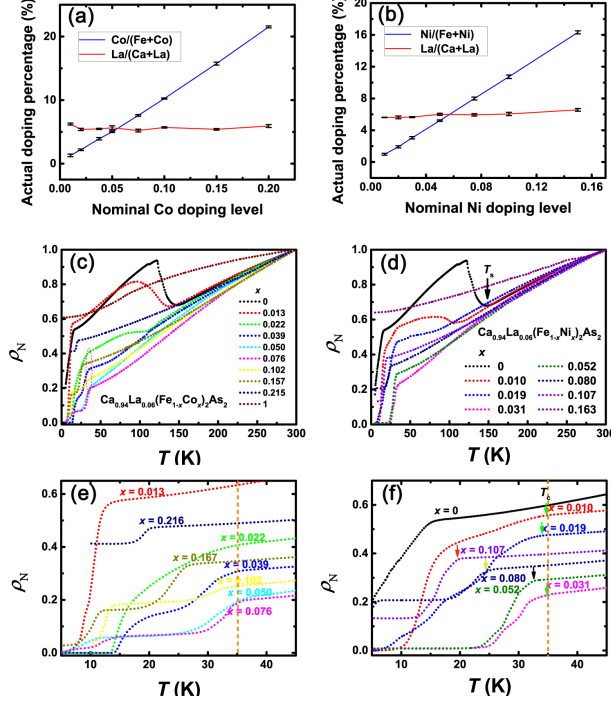


FIG. 1. (a-b) The actual doping level of TM (Co, Ni) and La determined by multi-point EDS measurement versus the nominal TM doping level. The error bars are the standard deviations among different measurements. (c-f) Temperature dependence of resistivity (RT) curves for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{TM}_x)_2\text{As}_2$ with various x . (e) and (f) are the enlarged views of the superconducting transition in RT curves.

the onset T_c is applied¹⁹. In all cases, after a sufficiently heavy electron doping (or equal effect with electron doping), the onset T_c is found to decrease linearly with x . The linear $T_c(x)$ suppression rates are -116.7 K/Fe and -223.8 K/Fe for Co and Ni substitution, respectively. In comparison with $\text{Ba}_{0.5}\text{K}_{0.5}(\text{Fe}, \text{TM})_2\text{As}_2$ (suppression rate: -173 K/Fe for Co, -221 K/Fe for Ni), the Ni suppression effect is comparable, while a weakened Co suppression effect is presented²⁰. On basis of the rigid-band model, substitution induced electron doping by Co and Ni is expected to be 1 e/Fe and 2 e/Fe, respectively. It is interesting to see that, the $T_c(n)$ curves for Co and Ni doping almost fall into one curve if the net doping electron number from both La and TM doping are taken into account. Both the range of the net doping electron concentration n that high- T_c SC appears and the T_c linear suppression region at heavy TM doping levels are almost identical to each other for Co and Ni substitutions, as shown in Fig. 2 (c). This behavior is in sharp contrast to that in TM-doped BaFe_2As_2 or

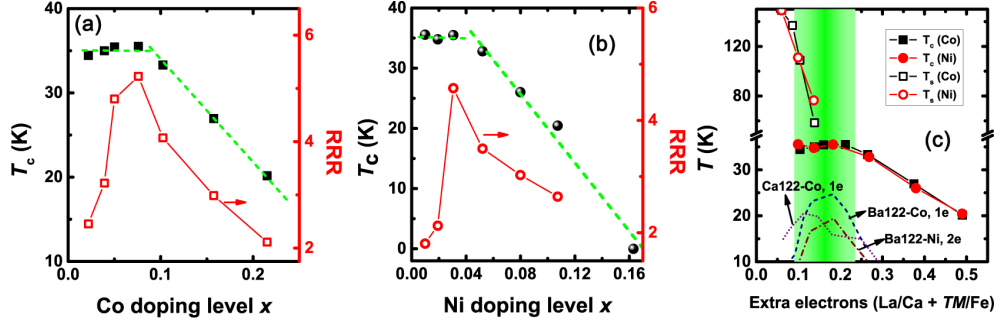


FIG. 2. (a-b) Superconducting transition temperature T_c and residual resistance ratio (RRR) plotted as functions of TM doping level x . (c) Superconducting and AFM transition temperatures (T_c and T_s) plotted as functions of the extra electron numbers (n) per unit cell induced by La and TM doping. Every substitution of La for Ca, Co for Fe, and Ni for Fe will introduce 1 e, 1 e, and 2 e, respectively. The dot, dash, and dot-dash lines in (c) represent the dome-shape electron doping dependent superconducting phase diagram for $\text{Ca}(\text{Fe}, \text{Co})_2\text{As}_2$, $\text{Ba}(\text{Fe}, \text{Co})_2\text{As}_2$, and $\text{Ba}(\text{Fe}, \text{Ni})_2\text{As}_2$ in ref.^{15,17,18}.

CaFe_2As_2 especially on the following two points^{15,21,22}. On one hand, in $\text{Ba}(\text{Fe}_{1-x}\text{TM})_2\text{As}_2$, since the number of electrons that participate in formation of Fermi surface (FS) is found to decrease from Co to Ni for a fixed nominal extra electron, mismatches among the $T_c(n)$ domes for different kinds of TM doping can be noticed. On the other hand, influenced by the different impurity potentials of the substituted atoms, the electronic structure is possibly changed and thus results in different T_c maximums. Therefore, the $T_c(x)$ constant behavior, the equal maximum T_c values, and the identical linear T_c suppression effect for Co and Ni doping under the rigid-band model are abnormal and unique properties only belonging to the present system.

To understand this unexpected carrier density independent T_c , we need to exclude possible experimental artifacts and pitfalls. Specifically, these three scenes, the phase separation, the chemical inhomogeneity, and the charge carrier cancelation effect, come in mind. First, we address the phase separation by systematic XRD and RT measurements. The XRD patterns for TM doping are shown in SI, S1. No crystalline phase separation can be observed. As expected, all (002 l) peaks gradually move toward higher values with increasing TM substitution for the smaller ion radius of Co and Ni than Fe. The phase separation interpretation should also be untenable in RT curve measurements. Supposing that $(\text{Ca}, \text{La})\text{Fe}_2\text{As}_2$

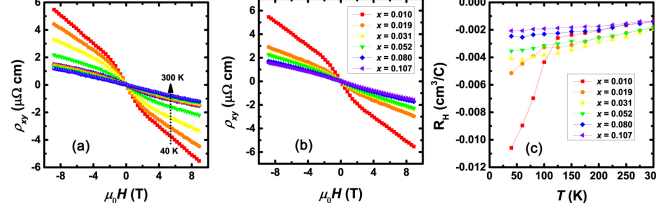


FIG. 3. (a) Magnetic field ($\mu_0 H$) dependence of Hall resistivity (ρ_{xy}) for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ with $x = 0.010$ at various temperatures. (b) Magnetic field dependence of Hall resistivity (ρ_{xy}) for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ with various doping levels ($0.010 \leq x \leq 0.107$) at $T = 40 \text{ K}$. (c) Temperature dependence of Hall coefficients (R_H) for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ at low field limits.

with unknown doping level shows the responsibility for the high T_c and the SDW/AFM transitions in RT curves are only associated to $\text{Ca}(\text{Fe}_{1-x}\text{TM}_x)_2\text{As}_2$, the resistivity upturn for SDW transition should persist up to doping level $x = 0.056$ for Co doping and $x = 0.053$ for Ni doping as in ref.^{15,22}. However, as shown in Figs. 1 (c) and (d), the disappearances of SDW transitions are much faster in both cases of Co and Ni doping, i.e., the electron concentration contributed by La doping is non-negligible.

To address the second point mentioned above, we emphasize on the elemental analysis. In Figs. 1 (a-b), the standard deviation is shown as the error bar of the actual doping level for every crystal. As can be seen, all error bars are almost too small to be distinguished, which means only small deviations occur among measurements on different points. A table listing raw data of EDS measurement for a typical doping level is provided in the SI, S1, Table I. One can notice the small deviations more intuitively. Given that there is an optimal doping level $x = p$ leading to the maximum T_c as many iron-based systems, we can determine the change strength of the doping-independent range as $(x_{\text{end}} - x_{\text{onset}})/2p$ where x_{onset} (x_{end}) is the onset (end) doping level in the T_c -constant region. If we define p as the middle of the doping level in this T_c -constant range, the change strength for Co and Ni is calculated to be 55% and 68%, respectively, which are far above the standard deviations (usually $< 0.2\%$) of the element La, the element TM, and even the both. For any element in crystals, no such large or even comparable deviation can be distinguished. Accordingly, we can conclude there is no elemental enriching effect or chemical inhomogeneity that is responsible for the carrier density independent T_c .

To address the charge carrier cancelation effect, we performed systematic Hall measurements on $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$. Fig. 3 (a) shows the magnetic field ($\mu_0 H$) dependence of Hall resistivity (ρ_{xy}) for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ with $x = 0.010$ at various temperatures. Below the SDW/AFM transition temperature T_s , the primary linear ρ_{xy} ($\mu_0 H$) at high temperatures becomes more and more concave. This behavior may be associated with emergence of mobile charge carriers with high mobility under the SDW transition²³. The H dependence of ρ_{xy} for $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ with different x at $T = 40$ K are displayed in Fig. 3 (b). The negative slopes indicate the dominant role of electrons in the transport behavior in all crystals. With increasing x , the absolute value of the negative slope gradually becomes small. The extracted Hall coefficients (R_H) at low field limit are plotted in Fig. 3 (c). For under-doping crystals ($x = 0.010, 0.019$), the SDW/AFM transition is also evidenced in $R_H(T)$ curves. Below T_s , R_H falls down quickly with decreasing T , which is a typical signature of the SDW transition observed in many iron-based compounds¹⁷. Since the high T_c starts from compound $x = 0.010$ for Ni doping, the existence of SDW state makes a much more drastic change of the electron concentration in this special T_c -constant range. This apparently rules out the possibility of the constant net mobile charge carrier (electron) for different x values due to unexpected electronic cancelation effect which may be resulted from As vacancies and other undesired factors^{11,24}. Consistent with the RT curves with continuous shape changes, we can conclude the concentration of the mobile charge carrier participating in transport varies drastically and continuously with x increasing.

The exclusion of the above three scenes is also supported by the smooth evolution of the residual resistance ratio (RRR) with doping. It should be noted out that, TM substitution behaves in dual roles, enhancement of impurity density and increasing of electron doping concentration. RRR in TM co-doping samples is a combined result of the scattering density and the mobile carrier concentration. If the transport influence from scattering density enhancement overcomes that from mobile carrier concentration increasing, RRR will increase. Otherwise, RRR will decrease. Due to this opposite influence of the scattering and the mobile carrier concentration on conducting ability, if any of the above three scenes exists, RRR will vary disorderly among different samples and even within samples in a same batch. In this case, no RRR regularity can be obtained. However, as can be seen in Figs. 2 (a) and (b), RRR changes orderly in both cases of Co and Ni substitutions, increasing in the T_c -constant region and decreasing monotonously in the linear $T_c(x)$ suppression region. In

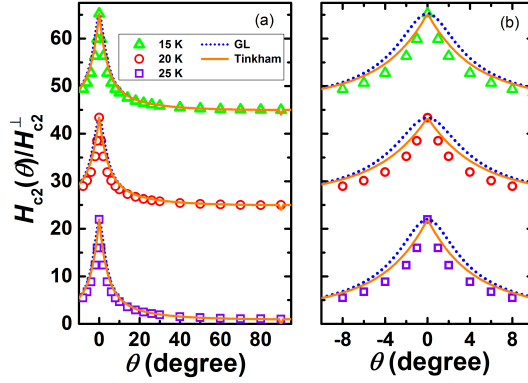


FIG. 4. (a-b) The angle θ dependence of the upper critical field H_{c2} in comparison with H_{c2}^{\perp} for temperatures at 15, 20, and 25 K for a $\text{Ca}_{0.94}\text{La}_{0.06}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ ($x = 0.052$) sample. θ is angle between the magnetic field orientation and the crystal surface. (b) is an enlarged view for θ near 0° . The solid lines represent the reproduced curves based on Tinkham (2D) and GL (3D) formula for angular-dependent H_{c2} using H_{c2}^{\perp} and H_{c2}^{\parallel} . For $T = 15$ K and 20 K (25 K), a criteria $\rho = 0.5\rho_N$ ($\rho = 0.9\rho_N$) is used to extract the $H_{c2}(\theta)$ values, where ρ_N is the normal state resistivity. The $H_{c2}(\theta)/H_{c2}^{\perp}$ curves for 20 K and 25 K are offset by 24 and 44 along y -axis.

fact, this evolution of $\text{RRR}(x)$ has been kept in many separated RT curve measurements (also in RT curves for $\text{Ca}_{1-x}\text{La}_x\text{Fe}_2\text{As}_2$, see SI, S3.). The initial RRR increase indicates that the effect of mobile carrier concentration increase wins the increase of impurity scattering in influencing transport. While at heavy doping side, the increase of impurity scattering wins the competition. The non-monotonous change of RRR with x increasing indicates a change of the dominated role in influencing transport from mobile carrier concentration to scattering density. Note that, the RRR decrease at heavy doping levels for all cases coincide with the start of linear $T_c(x)$ suppression.

The unexpected charge carrier density independent T_c is very similar to the situation in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ - La_2CuO_4 bilayer in which the superconductivity comes from the interface⁴. If the proposed interface SC origin for the high T_c is the right interpretation, one should find the related evidences of 2D SC. As is known, for sufficiently thin superconducting films with thickness d satisfying $d \ll \xi_c$, Tinkham's formula for angular dependence of the upper critical field H_{c2} is satisfied. Here ξ_c is the c -axis coherence length. The Tinkham's formula

is expressed as¹²

$$\left| \frac{H_{c2}(\theta)\sin\theta}{H_{c2}^{\perp}} \right| + \left(\frac{H_{c2}(\theta)\cos\theta}{H_{c2}^{\parallel}} \right)^2 = 1. \quad (1)$$

θ is angle between the magnetic field orientation and crystal surface, and H_{c2}^{\perp} (H_{c2}^{\parallel}) is upper critical field with field perpendicular (parallel) to the crystal's surface. For 3D bulk superconductors, the angle dependence of H_{c2} can be interpreted by the Ginzburg-Landau (GL) anisotropic mass model with formula $H_{c2}(\theta) = H_{c2}^{\parallel}(\cos^2\theta + (H_{c2}^{\parallel}/H_{c2}^{\perp})^2\sin^2\theta)^{-0.5}$, which has been frequently applied in IBSs²⁵. The most remarkable difference between two models is the slope $|dH_{c2}/d\theta|$ value when $\theta \rightarrow 0^\circ$. Under Tinkham's model, $|dH_{c2}/d\theta|$ near $\theta \rightarrow 0^\circ$ is a finite value while it approaches zero in the GL model. We have accordingly measured the resistivity as a function of magnetic field for different field orientations at three selected temperatures below T_c and extracted the angle-dependent H_{c2} using different H_{c2} criteria (see Figs. 4). For field orientation close to crystal's surface, the spaced angle interval has been set closely as 1° . A cusplike behavior for θ near 0° is observed in $H_{c2}(\theta)$ curves (see Fig. 4 (b)). As expected, 2D Tinkham's model reproduces $H_{c2}(\theta)$ much better than 3D GL model. $|dH_{c2}/d\theta|$ near 0° slightly falls below Tinkham interpolation curve which is common to the Nb/Cu samples in the 2D region²⁶. In Nb/Cu multilayers, the $H_{c2}(\theta)$ curve near $\theta \rightarrow 0^\circ$ shows a transformation from a cusplike shape to a rounded shape continuously induced by the thickness (d_{Cu}) change of the Cu layer, from $\xi_c = d_{\text{Cu}}$ to $\xi_c = 6d_{\text{Cu}}$. Therefore, analogically, the superconducting layers in the present system are well separated by non-superconducting region with distance at least comparable to ξ_c along c -axis. Therefore, the high- T_c superconductivity is two-dimensional in nature. The further evidences verifying the 2D nature of the high- T_c superconductivity from angle-resolved magneto-resistance measurements will be shown in SI, S4.

Recently, two different groups have suggested that the high- T_c superconductivity in (Ca, RE)Fe₂As₂ may originate crystalline defects from RE dopants^{11,24}. Under such scene, the abrupt occurrences of defects and high- T_c superconductivity are still very elusive. In fact, it is argued in ref.²⁷ that the Pr dopants in the same compounds Ca_{1-x}Pr_xFe₂As₂ do not cluster, but repel each other at short length scales. In the present case, one can naturally speculate that Co and Ni doping are uniform as the case in Ba(Fe, TM)₂As₂. Then, both Co and Ni doping only induce extra electrons but not promote formation of RE defects. If the idea of defect origin for superconductivity is true, we can conclude that in low- x

$\text{Ca}_{1-x}\text{RE}_x\text{Fe}_2\text{As}_2$ without high- T_c , RE defects already exist. There must have an enough electron concentration for high- T_c occurrence. That is, sufficient electron doping is necessary. Our present data strongly support the conjecture that the unusual enhancement of superconductivity in $(\text{Ca}, \text{RE})\text{Fe}_2\text{As}_2$ in comparison with its counterparts may be closely related to some kind of interfacial effect, which is consistent with the recent manifestation of non-negligible interfacial effect on the occurrence of 100 K superconductivity in FeSe monolayer²⁸, in which the charge transfer from substrate also contributes to the high- T_c . Note that, it is theoretically predicted that quantized superconducting temperature and doping levels could occur in interface superconductivity⁸. Whether there is a correlation between this quantized behavior and the observed T_c constant phenomenon is still an open question.

In summary, we have investigated the TM element substitution effect on the high- T_c superconductivity in $(\text{Ca}, \text{La})\text{Fe}_2\text{As}_2$ compound. The onset high T_c has been found to keep almost invariable for a large range of electron doping. Through systematic structural/elemental and transport analyses, the extrinsic scenes, namely the phase separation, the chemical inhomogeneity, and the charge carrier cancellation effect, have been excluded. Additionally, the two-dimensional nature of the high- T_c superconductivity has been verified by magnetic field and angular dependent transport measurements. The present results give strong supports for the interface-effect-induced high- T_c superconductivity in iron pnictides and provide opportunity for exploring new perspective in understanding of especially interface-effect-induced superconductivity.

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